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PHYSICAL PROPERTIES OF CRYSTALS

Instability of the Local Environment of Mn^{2+} in BaF_2

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Abstract—Excitation and luminescence spectra and luminescence lifetime of Mn^{2+} ion in BaF_2 crystals at 77 K have been investigated for the first time. Mn^{2+} ions in the crystal are coordinated by six and eight fluorine ions, have a trigonal environment, and form exchange-coupled pairs. Several types of centers of the Mn^{2+} ion are formed mainly because of the large difference in the Mn^{2+} and Ba^{2+} ionic radii, which causes instability of the local structure around the activator and its strain, and exchange striction. An increase in the impurity concentration enhances these factors, thus changing the relative concentration of various centers.

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INTRODUCTION

According to the electron spin resonance (ESR) data, the Mn^{2+} ion in $MeF_2:Mn^{2+}$ crystals (*Me* = Cd, Ca, Sr, or Ba) is incorporated into the center of a cube with fluorine ions at vertices, whereas in CaF_2, SrF_2, and BaF_2 crystals Mn^{2+} ions form exchange-coupled pairs Mn^{2+}–Mn^{2+} [1–4]. In addition, trigonal centers were found in $SrF_2:Mn^{2+}$ and $BaF_2:Mn^{2+}$ crystals [5, 6]. Since the properties of 3*d* ions depend on the environment, one would expect these centers to manifest themselves in optical spectra as well. The optical spectroscopy of $CaF_2:Mn^{2+}$ crystal has been reported in detail. This crystal is widely used in thermoluminescence dosimetry. At the same time, there is a problem referred to as the zero-dose problem [7, 8]. After storing in darkness, a dosimeter that was not subjected to ionizing radiation exhibits a dose of about 0.1 mGy or higher (depending on the sample history), which exceeds the natural background. The reason for this persistent effect is the absence of clear information about the mechanism of thermoluminescence, formation of defects, and their stability in crystals [9]. Finding the reasons for the defect formation in other uninvestigated terms of the $MeF_2:Mn^{2+}$ series should helt to solve this problem. In this context, $BaF_2:Mn^{2+}$ crystals are the most interesting objects. In this paper, we report the results of studying the photoluminescence (PL) of $BaF_2:Mn^{2+}$.

EXPERIMANTAL

The samples were grown by the Bridgman method in a fluorine atmosphere with manganese additives in the form of MnF_2. The experiments were carried out on a SKAN-1 system. The excitation source was a xenon lamp; FEU-106 and FEU-62 photoelectron multipliers were used as photodetectors. Spectra of stationary and sampling (with a delay time of 1 ms) luminescence were measured in the range of 400–900 nm. The stationary PL is considered to be sampling luminescence excited by a constant-radiation source without modulation. Only the signal of the mean equilibrium PL of the centers of the object under study is modulated. The nonstationary (sampling) PL is obtained by modulating the excitation radiation and detecting the afterglow with a phase shift. Two modulators are used in this case: after the excitation source and before the monochromator input slit. A joint analysis of the spectra recorded by these two methods makes it possible to reveal centers with luminescence kinetics differing by three (or even larger) orders of magnitude. To determine the fluorescence lifetime, we applied the zero-phase technique using a lock-in detector [10] and directly recorded the phosphorescence decay kinetics. When measuring excitation spectra (ESs), the emission band was selected by a filter or monochromator. The experiments were performed at $T = 77$ K.

RESULTS

PL spectra of $BaF_2:Mn^{2+}$ crystals contain no less than five bands, which can be explained by the presence of several centers in the system (Fig. 1). The spectra recorded by the sampling method contain mainly the 547-nm band (curve *1*) for $C_{Mn} = 0.1\%$ and only the 594-nm band (curve *3*) for $C_{Mn} = 0.5\%$ (C_{Mn} is the manganese ion concentration). These bands are due to two centers: Mn_I and Mn_{II}, respectively.

The ESs of the centers are shown in Fig. 2 (curves *3*, *4*). These spectra differ significantly in two